Electrical Properties and Superconductivity of Rhenium and Molybdenum Films*

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Electrical and superconducting properties of rhenium and molybdenum films prepared by electron beam evaporation have been measured as a function of substrate temperature, film thickness, and substrate material. The films were prepared at residual pressures of 5×10^{-8} Torr. In addition, films of each material were prepared by reactive deposition at nitrogen pressures in the 10^{-5} Torr range. Rhenium films prepared at low residual pressures exhibited superconductivity with onset temperatures from 2.5–4.9 K depending on thickness and substrate temperature. However, rhenium films prepared by reactive deposition in nitrogen had onset temperatures from 4.6–5.5 K. Transition temperatures from 3.3–3.8 K were observed in molybdenum films at thicknesses greater than 6000 Å when deposited at substrate temperatures of 600°C. Crystal structure and preferred orientation were determined by x-ray diffraction methods.

Introduction

Enhanced superconducting transition temperatures have been reported in both rhenium and molybdenum films prepared by evaporation and sputtering.[1–3] These higher transition temperatures compared to the bulk material have been attributed to structural and impurity effects. The purpose of this investigation was to gain an understanding of the enhanced transition temperatures obtained in these materials by film growth methods that have been used to obtain nearly bulk material properties in other transition metals.[4,5] The electrical and superconducting properties of rhenium and molybdenum films deposited at low residual pressures were examined as a function of substrate material, substrate temperature, and film thickness. A comparison was made between films prepared under high purity growth conditions and those prepared by reactive deposition in nitrogen. Crystal structure was determined by x-ray diffraction. As a result of the study, we believe our observed enhanced transition temperatures are due primarily to strain effects rather than impurity effects.

I. Film Preparation

An electron beam gun with a maximum input power of 3 kW was used to deposit the films from high-purity-zone refined materials. Two vacuum systems were used to compare film properties. One was an oil diffusion pumped system equipped with a liquid-nitrogen trap. The other one was an ion pumped system. Both evaporator systems were equipped with Meissner traps cooled by flowing liquid nitrogen. The films were prepared at a total residual pressure of 5×10^{-8} Torr with the N_2 partial pressure monitored at $<10^{-10}$ Torr and water partial pressure at $<3\times10^{-10}$ Torr. Several cleanup runs using the gettering action of these reactive materials were usually made in order to achieve the ultimate background pressure. Three sets of films were prepared at different substrate temperatures in each vacuum cycle by the use of a rotary substrate carrier. Each set included a substrate of Corning 7059 glass, fused quartz, and sapphire. The controlled substrate temperatures were varied between 25° and 600°C. The pressure during evaporation was $3–5\times10^{-7}$ Torr while evaporating at full input power. Deposition rates were typically 20 Å/sec for rhenium and 100 Å/sec for molybdenum. Previously, using the same film growth methods, superconducting films of niobium, vanadium, and tantalum were obtained with superconducting transition temperatures near the bulk material values (within a few tenths of a degree). In addition to the comparison of the properties of the films prepared in different evaporators, comparisons were made of film properties by permitting the background and evaporating pressure to vary a factor of 10 from the high vacuum conditions.

II. Film Properties

Film properties were determined as a function of film thickness, substrate material, and substrate

temperature. Four-terminal resistance measurements were made at 300 K, 77 K, and below 10 K. From 10–4.2 K measurements were made in thermally controlled liquid-helium vapor using a calibrated carbon resistor thermometer. From 4.2–1.3 K measurements were made in a liquid-helium bath using vapor pressure as the thermometer. Measurements were not extended below 1.3 K.

For the purposes of this discussion, the temperature of the initiation of the superconducting transition was identified as T_c, and T_c was defined as the temperature at which the resistance was 10% below its normal value. The transition width, ΔT_c, was taken as the 10%–90% width of the resistance transition.

A. Rhenium

Rhenium films ranging from 125–4600 Å thick for 400°C and 600°C substrate temperatures were examined on all substrates. Only noncontinuous, cracked films were obtained for substrate temperatures below 400°C. The upper limit of the substrate heater was 600°C. Furthermore, depending on substrate material, thicker films were similarly cracked at all substrate temperatures.

The electrical properties of these rhenium films for only sapphire substrates are summarized in Table I, since film properties were found to be independent of substrate material. Except for very thin films the 600°C films showed better properties than the 400°C films. However, under no conditions did these electrical properties approach those of the bulk material. The bulk properties are also given in Table I for comparison purposes.

As seen in Table I, the lowest transition temperatures observed were between 2.5 and 2.8 K for medium thickness films of order 1000 Å while T_c increased appreciably for thin and thick films. Corresponding to the high transition temperatures are large transition

TABLE I. Electrical properties of rhenium films: ρ resistivity, $\mu\Omega$-cm; $R300$ K/$R10$ K, resistance at 300 K/resistance at 10 K; α temperature coefficient of resistance, ($R300$ K$-R77.3$ K/($R77.3$ K$\times 223$). T_c, superconducting transition temperature, K; ΔT_c, superconducting transition width, K.

		SAPPHIRE SUBSTRATES					
THICKNESS Å	SUBSTRATE TEMP °C	ρ 300°K $\mu\Omega$CM	R300°K / R10°K	TCR(α) $^\circ C^{-1} \times 10^4$	$\rho\cdot\alpha$ $\mu\Omega CM\,^\circ C^{-1}$	Tc °K	ΔTc °K
125	400	63	1.97	45	0.28	4.17	0.64
300	600	66	2.08	34	0.22	3.31	0.60
	400	61	3.47	31	0.19	2.58	0.04
700	600	46	2.43	43	0.20	2.80	0.05
	400	60	3.11	27	0.16	2.48	0.12
1600	600	33	3.41	66	0.22	2.63	0.05
	400	71	1.87	28	0.20	2.49	0.03
3200	600	34	2.47	45	0.15	2.69	0.10
	400	59	2.39	42	0.25	4.52	
4600	600	40	2.91	56	0.23	4.35	
	400	74	2.29	30	0.22	4.92	0.97
BULK PROPERTIES		18.7		325	0.61	1.7	

TABLE II. Properties of films evaporated in nitrogen.

		SAPPHIRE SUBSTRATES					7059 GLASS SUBSTRATES	
THICKNESS Å	SUBSTRATE TEMP°C	ρ300°K $\mu\Omega$CM	R300°K / R4.2°K	TCR (α) $^\circ C^{-1} \times 10^4$	$\rho\cdot\alpha$ $\mu\Omega CM\,^\circ C^{-1}$	Tc °K	R300°K / R4.2°K	TCR (α) $^\circ C^{-1} \times 10^4$
400	25	83	1.18	7.0	0.058		1.17	7
	200	40	1.38	15	0.059		1.36	14
	400	30	1.44	17	0.049		1.47	18
	600	9	3.28	75	0.068		1.98	37
1200	200	36	1.37	14	0.051		1.36	14
	400	32	1.45	17	0.054		1.44	17
	600	9	2.72	57	0.054		2.21	43
3600	25	NON-ADHERENT					1.23	9
	400	19	1.73	27	0.052		1.74	28
	600	7	5.66	133	0.093		2.29	47
6000	25	NON-ADHERENT					1.14	5
	200	34	1.33	15	0.052		1.46	18
	400	21	1.78	28	0.060		1.68	26
	600	9	3.76	87	0.082	3.36	2.29	47
21,000	600	6	3.87	88	0.050	3.78	2.63	45
BULK PROPERTIES		5.3		358	0.19	0.92		

widths. Variation of background pressure, evaporation pressure, or evaporation system did not effect the observed T_c. At no time was the T_c reported for high purity, well-annealed bulk rhenium obtained.

The transition temperatures initially measured were stable to recycling over short term periods of a month. However, on re-examination after one year original T_c values of 2.5–2.8 K had remained the same, while the T_c of the thick and thin films had relaxed down to the 2.5–2.8 K range with the corresponding resistance vs temperature curve.

B. Molybdenum

Molybdenum films were examined in the thickness range from 400–21 000 Å for 25°–600°C substrate temperatures and all substrate materials. Depending upon substrate material, films deposited on 25°C substrates or made very thick were cracked.

The electrical properties of the continuous films for sapphire and Corning 7059 glass are summarized in Table II. The properties of the films on fused quartz were nearly identical with those on Corning 7059 glass. The film properties were better for sapphire than Corning 7059 glass. Furthermore, there was a significant improvement on sapphire substrates at a substrate temperature of 600°C. However, even for this case the bulk properties were not achieved.

Since the bulk transition temperature (0.92 K) is well below our measuring range, we were unable to fully examine the superconducting properties of the molybdenum films. However, for films thicker than 6000 Å we were able to see an enhanced transition almost four times the bulk transition temperature.

C. Films Evaporated in Nitrogen

Films of both rhenium and molybdenum were prepared by depositing in a nitrogen atmosphere controlled to 5×10^{-5} Torr in order to compare their properties with those prepared at a total residual pressure of 5×10^{-8} Torr. The properties of these

films are summarized in Table III. All of these films had electrical properties further from the bulk values than the corresponding high-vacuum films. The reactively deposited rhenium films of medium thickness had superconducting transition temperatures more than twice as great as the rhenium films prepared under high purity conditions for corresponding conditions of thickness and substrate material. After a year's time, these high transition temperature films had annealed to a much broader transition beginning at approximately the same high temperature (with about the same T_c) but now extending to a lower temperature of about 2.5 K. The reactively deposited thick molybdenum film was just barely beginning its superconducting transition at 1.3 K.

III. X-Ray Diffraction Measurements

The x-ray analysis results of high purity and reactively deposited rhenium films are summarized in Table IV. Only the normal rhenium pattern was observed for high purity films approximately 1000 Å thick although the measured lattice parameters generally differed from the bulk values of $a_0=2.760$ Å and $c_0=4.458$ Å by more than the measurement error of ± 0.005 Å. For the reactively deposited film of corresponding thickness a modified structure was found with other lines in this pattern fitting a simple cubic structure. The grain size obtained from the x-ray diffraction pattern is also shown in Table IV and varied from about 700 Å for the high purity films to 200 Å for the reactively deposited films.

The diffraction data for the molybdenum films are summarized in Table V. For high purity films up to 3400 Å thick a normal pattern was observed while for thicker films other lines appeared. Again the measured lattice parameter differed from the bulk value of $a_0=3.147$ Å by more than the measurement error of ± 0.005 Å for approximately 1000-Å-thick films. However as the films became thicker this lattice parameter deviation decreased and the other lines appeared. For thick reactively deposited molybdenum a modified structure was observed. The grain size is also shown in Table V and varied from 200–135 Å for high purity films of thickness 400–5800 Å. Furthermore, for the thick reactively deposited film the grain size was 115 Å.

TABLE III. Properties of films evaporated in nitrogen.

SUBSTRATE MATERIAL	THICKNESS Å	SUBSTRATE TEMP °C	$\rho_{300°K}$ μΩ CM	$\frac{R_{300°K}}{R_{10°K}}$	TCR (α) $°C^{-1} \times 10^4$	T_c °K	ΔT_c °K
RHENIUM							
SAPPHIRE	1400	400	83	1.41	17	5.47	0.92
7059 GLASS	1400	400	130	1.49	16	4.65	1.0
SAPPHIRE	700	400	98	1.37	13	5.30	1.0
7059 GLASS	700	400	100	1.42	13	4.74	0.80
MOLYBDENUM							
SAPPHIRE	10,000	400	44	1.03	16	--	--
7059 GLASS	10,000	200	575	0.94	-51	--	--

TABLE IV. X-ray diffraction measurements of rhenium films.

T_c °K	THICKNESS Å	SUBSTRATE TEMP °C	SUBSTRATE MATERIAL	UNIT CELL Å a_0	UNIT CELL Å c_0	ORIENTATION INTENSITY (101)	(100)	(002)	OTHER LINES	GRAIN SIZE Å
RHENIUM (BACKGROUND PRESSURE 5 X 10^{-8} TORR)										
2.49	1300	400	α-Al_2O_3	2.748	4.440	26	2.4	1.0	--	
			SiO_2	2.751	4.450	7.0	2.5	1.0	--	1000
			7059 GLASS	2.765	4.462	6.8	2.8	1.0	--	
2.80	700	600	α-Al_2O_3	2.744	4.450	13.2	10	1.0	--	700
2.63	1650	600	7059 GLASS	2.744	4.444	9.7	3.9	1.0	--	700
RHENIUM (EVAPORATED IN NITROGEN AT 5 X 10^{-5} TORR)										
4.74	700	400	7059 GLASS	2.749	4.440	--	4.7	1.0	5.33, 2.67 1.78, 1.33 THESE FIT A SIMPLE CUBIC SYSTEM	190

TABLE V. X-ray diffraction measurements of molybdenum films.

THICKNESS Å	SUBSTRATE TEMP °C	SUBSTRATE MATERIAL	UNIT CELL Å a_0	ORIENTATION INTENSITY (110)/(211)	OTHER LINES	GRAIN SIZE Å
MOLYBDENUM (BACKGROUND PRESSURE 5 X 10^{-8} TORR)						
1400	600	α-Al_2O_3	3.136	0.5	--	200
400	600	α-Al_2O_3	3.136	3.2	--	160
3400	400	SiO_2	3.146	38.5	--	160
5800	200	SiO_2	(211) - 3.145 (220) - 3.139	29.4	(220)	135
MOLYBDENUM (EVAPORATED IN NITROGEN AT 5 X 10^{-5} TORR)						
17,000	400	SiO_2	(211) - 3.145 (220) - 3.148	4.5	(200) (220)	115

IV. Discussion

A. Rhenium

X-ray examination of high purity films approximately 1000 Å thick showed a lattice parameter deviation but no structural change from that of bulk rhenium. T_c was between 2.5 and 2.8 K—appreciably higher than the bulk value of 1.7 K.

Films approximately 1000 Å thick reactively deposited in nitrogen at 5×10^{-5} Torr had transition temperatures of about 5 K and x-ray analysis showed both ordinary rhenium structure and other lines (presumably the nitride). However, variations by a factor of 10 in background and evaporation pressure (and all partial pressures) for the high purity films gave no change in T_c which one would expect if the 2.5–2.8 K transition temperatures were due to impurities.

In addition to the strain indicated by the lattice parameter deviation, extreme strain effects, i.e., cracking of films, were observed for substrate tempera-

tures below those of the examined films and for thicker films at all substrate temperatures. Since T_c increased with film thickness it varied essentially as film strain. Furthermore, long term stability of the films showed that T_c for the thick and thin films relaxed down to the 2.5–2.8 K temperature range from above 4 K, whereas the reactively deposited films annealed, but did not relax in the same way.

Grain size measurements showed a difference between high purity and reactively deposited films of comparable thickness, however, the grain size in all cases was too large to give the transition temperature effects observed.

B. Molybdenum

X-ray analysis examination of high purity films showed a lattice parameter deviation for approximately 1000-Å-thick films which was relieved for thicker films as a structural change occurred. In addition extreme strain, i.e., cracking of very thick films was observed. Since measurements of T_c were limited to above 1.3 K, transition temperatures were observed only for thick films ($\geq$6000 Å) in agreement with a strain induced enhancement of T_c.

In thick films reactively deposited in nitrogen at 5×10^{-5} Torr, the superconducting transition was just beginning at 1.3 K in contrast to a T_c of 3.5 K for corresponding high purity films.

Grain size measurements varied very little over a large thickness range for the high purity and reactively deposited films. Again the grain size was too large to effect T_c to the degree observed and was inconsistent with the dependence of T_c.

C. Conclusion

Consequently, all evidence indicates that the primary enhancement mechanism for our high purity rhenium and molybdenum films was strain, rather than impurity effects. Our results are in agreement with the observation that large intrinsic stresses are found in deposited films for metals having high melting temperatures and high shear moduli.[6] However, in the very high transition temperature case there is a structural change associated with the large strains as indicated by the x-ray patterns of the thick molybdenum films.[2] Grain size measurements indicate that in this particular study grain size was not important in the transition temperature enhancement.

It is interesting to note that for Nb, V, and Ta high purity films evaporated the same way with similar film parameters (purity, thickness, and grain size) it was found that thick films ($\gtrsim$6000 Å) had transition temperatures essentially of the pure bulk metal (within a few tenths of a degree). For these thick films the electrical properties approximated the pure bulk metal values better than any of the present rhenium or molybdenum high purity films. For example, the temperature coefficient of resistance (TCR) for Nb, V, and Ta came within a factor of 2 of the bulk value while for rhenium and molybdenum the TCR was always greater than a factor of 5 from the bulk value. Hence, if films of rhenium and molybdenum could be evaporated without change of crystal structure with electrical properties as near the bulk material, they also should have the bulk T_c.

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References

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1. W. C. Bond *et al.*, Phys. Rev. Letters **15**, 260 (1965).
2. K. C. Chopra, Phys. Letters **25A**, 451 (1967). K. C. Chopra *et al.*, Phil. Mag. **25A**, 261 (1967).
3. J. R. Gavalier *et al.*, Bull. Am. Phys. Soc. **13**, 730 (1968); J. R. Gavalier *et al.*, J. Vac. Sci. Technol. **6**, 177 (1969).
4. P. E. Friebertshauser and L. B. Leder, J. Vac. Sci. Technol. **4**, 335 (1967) (presented at the 14th Natl. Vac. Symp., Kansas City, 1967).
5. P. E. Friebertshauser and J. W. McCamont, J. Vac. Sci. Technol. **6**, 184 (1969).
6. E. Klokholm and B. S. Berry, J. Electrochem. Soc. **115**, 823 (1968).